Lattice dynamical study of alkali metals: An unified approach based on CGW model

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Abstract. The phonon dispersion relations for lithium, sodium, potassium, rubidium and cesium along the principal symmetry directions as well as their lattice specific heats have been deduced using Clark, Gazis and Wallis angular force model. This model which conforms to the translational symmetry of the lattice, reproduces the observed crossover in lithium along [$\zeta 00$] direction at $\zeta = 0.49$, without producing any crossovers in other alkali metals. Besides, the theoretical dispersion curves of all alkali metals are in excellent agreement with the corresponding experimental or homologous dispersion relations and their θ_D values compare well with the experimental values over a wide temperature range. It is shown that the strength of electron-ion interactions plays a significant role in the success of any unified lattice dynamical study of alkali metals while the three-body interactions of the CGW model do not. The importance of umklapp processes, failure of the earlier models to produce a crossover and the experimental θ_D–T curve in lithium as well as the apparent variation in the nature and range of atomic interactions of alkali metals are discussed.

1. Introduction

Over the past few years, the lattice dynamics of alkali metals has been investigated extensively on the basis of central force models (Sharma and Singh 1972; Das *et al* 1977), Delaunay angular force (DAF) models (Tripathi and Behari 1971; Jogi 1974; Sharma and Awasthi 1979), Clark, Gazis and Wallis angular force (CGW) models (Prakash *et al* 1974; Goel *et al* 1975; Kushwaha and Kushwaha 1980), axially symmetric force (AS) models (Dacunha Lima *et al* 1974; Rai and Hemkar 1977; Khanna and Rathore 1979), general tensor force (GTF) models (Bonelli and Shukla 1977; Bonelli *et al* 1979) and other models (Rathore and Verma 1977; Ramji Rao and Rajput 1981) as well as a variety of pseudopotential models (Animalu *et al* 1966; Ho 1968; Prakash and Joshi 1969; Price *et al* 1970; Gurskii and Krasko 1971; Soma 1980; Sen and Sarkar 1981). In addition, the phonon frequencies of lithium (Smith *et al* 1968), sodium (Woods *et al* 1962), potassium (Cowley *et al* 1966) and rubidium (Copley and Brockhouse 1973) have been measured using the inelastic scattering of neutrons. Nevertheless, it is not at all clear from these investigations whether a general lattice dynamical model is capable of reproducing the experimental dispersion curves of all alkali metals or whether the nature and range of atomic interactions vary from one alkali metal to another. For

instance, all the phenomenological models mentioned above reproduce the experimental phonon frequencies of sodium and potassium along the principal symmetry directions but fail to produce a crossover in lithium along the $[\zeta 00]$ direction. Other models (Sharan *et al* 1973; Singh *et al* 1976; Gohel and Jani 1979) which produce a crossover in lithium, would produce similar crossovers along the $[\zeta 00]$ direction in sodium and potassium. Even some of the pseudopotential models (Ho 1968; Prakash and Joshi 1969; Gurskii and Krasko 1971; Soma 1980; Sen and Sarkar 1981) have not succeeded in reproducing the crossover in lithium. Besides, the experimental phonon frequencies of rubidium have not been reproduced at several wavevectors and polarizations by many force constant models (Sharma and Singh 1972; Cavalheiro and Shukla 1974; Goel and Dayal 1977; Khanna and Rathore 1979) while those of cesium are not available to judge the capability of the other models (Sharma and Singh 1972; Jogi 1974; Sharma and Awasthi 1979).

On the contrary, the degree of homology exhibited by the experimental phonon frequencies of lithium, sodium, potassium and rubidium is not consistent with any variation in the nature and range of their interatomic forces. Ramamurthy and Satishkumar (1978, 1980) have shown by analysing these phonon frequencies that the observed crossover of the $[\zeta 00]$ branches in lithium is not an anomalous property, but manifests itself only in alkali metals of smaller atomic mass and interatomic distance while it degenerates into overlapping in others. For the first time, these authors (Ramamurthy and Satishkumar 1981) have deduced a reliable set of phonon frequencies of cesium along the principal symmetry directions which are homologous with the corresponding experimental frequencies of other alkali metals. Besides, Ramamurthy and Singh (1978) and Satishkumar (1981) have succeeded in reproducing the crossover in lithium with a large positive value of the electron gas constant, C' by making use of five constant and six constant AS models, respectively. These models which satisfy the symmetry requirements of the lattice did not produce a crossover of dispersion curves in any other alkali metal. On the other hand, the crossovers produced by the previous models (Sharan *et al* 1973; Singh *et al* 1976; Gohel and Jani 1979) with a negative C' value are a consequence of artificially matching the results of a phenomenological model with no translational symmetry with those of experiments which conform with the symmetry of the lattice and hence have no physical significance (Ramamurthy and Neelakandan 1977).

In order to ascertain the differences in the nature and range of their interatomic forces as well as to understand the circumstances under which the dispersion curves of an alkali metal crossover, it is of crucial importance to investigate the lattice dynamics of all alkali metals using a model which is consistent with the translational symmetry requirements of a lattice. A detailed analysis of various lattice dynamical models has established that the CGW model which incorporates some three-body interactions, is unique and not equivalent to any other model (Ramamurthy 1982). The present authors have therefore made use of a CGW model which includes the volume forces separately, to investigate the lattice dynamics of all alkali metals and to determine whether the three-body interactions are in any way responsible for the observed crossover in lithium. This paper describes an unified approach to phonon dispersion relations and lattice specific heats of alkali metals and reveals the nature of the interatomic forces responsible for a crossover of dispersion curves along the $[\zeta 00]$ direction.

2. Theory

2.1 *Secular determinant*

The secular determinant for the phonon frequencies of the crystal is

$$|D(\mathbf{q}) - \omega_{\mathbf{q}}^2 \hat{I}| = 0, \tag{1}$$

where $\omega_{\mathbf{q}}$ is the phonon frequency associated with the wavevector, $\mathbf{q}$ and $\hat{I}$ is a 3×3 unit matrix. Assuming that the atomic interactions in alkali metals could be expressed in terms of central, angular and volume forces, the dynamical matrix $D(\mathbf{q})$ is split into three parts as

$$D(\mathbf{q}) = D^r + D^l + D^e, \tag{2}$$

where D^r and D^l represent the contributions arising from central and angular forces, respectively, to the short range ion-ion interactions and D^e represents the contributions from volume forces to the long range electron-ion interactions. If the range of the central force interactions is extended up to third nearest neighbours, the elements of the matrix D^r, obtained by straightforward calculations, could be written as

$$
\begin{aligned}
MD_{xx}^r &= \tfrac{8}{3}\beta_1 [1 - C_x C_y C_z] + 4\beta_2 S_x^2 + 2\beta_3 [2 - C_{2x}(C_{2y} + C_{2z})], \\
MD_{xy}^r &= \tfrac{8}{3}\beta_1 S_x S_y C_z + 2\beta_3 S_{2x} S_{2y},
\end{aligned} \tag{3}
$$

where $S_x = \sin(q_x a/2)$, $S_{2x} = \sin(q_x a)$, $C_x = \cos(q_x a/2)$ and $C_{2x} = \cos(q_x a)$ etc., M is the mass of the ion, β_n is the nth neighbour central force constant and a is the lattice parameter.

Angular forces in the cGW model (Clark *et al* 1964) arise from the resistance of the angles of a triangle formed by joining three lattice points to deformation and are invariant under rigid body rotations. The total angular energy, however, should include the self-consistent set of triangles comprised of all combinations of interatomic distances up to the largest one considered. If the range of these interactions is restricted to the first three neighbours, the isosceles triangles of types I and II and the equilateral triangles of type III, formed by joining an atom with its first neighbours separated by second neighbour distance, first and second neighbours separated by first neighbour distance and third neighbours separated by third neighbour distance, respectively, constitute a complete set. There are, with reference to an atom at the origin, 12 triangles of type I, 24 triangles each of types II and III in this set. The first, second and third neighbour distances subtend angles θ_2, θ_1 and θ_3, respectively, in these triangles. The elements of the matrix D^l, obtained by summing over these three angles in the set are given by (Satishkumar 1983)

$$
\begin{aligned}
MD_{xx}^l &= \tfrac{8}{3}(4\gamma_1 + 6\gamma_2)[1 - C_x C_y C_z] + \tfrac{8}{3}\gamma_1 [4S_x^2 - S_y^2 - S_z^2] \\
&\quad + 4\gamma_2 [S_y^2 + S_z^2] + 3\gamma_3 [3 - C_{2x}C_{2y} - C_{2y}C_{2z} - C_{2z}C_{2x}], \\
MD_{xy}^l &= -\tfrac{8}{3}(2\gamma_1 - 3\gamma_2)S_x S_y C_z + \tfrac{3}{2}\gamma_3 S_{2x} S_{2y}.
\end{aligned} \tag{4}
$$

where γ_n is the angular force constant associated with the angle θ_n. These force constants have been divided by a normalizing factor $3a^2/4$, in order to make them dimensionally equal to the central force constants.

The volume forces which owe their origin to the presence of conduction electrons, are

expressed in terms of the deformation potential. When the exchange and correlation effects are taken into account through an appropriate screening function, the elements of the matrix D^e which include the contributions from umklapp processes are given by (Ramamurthy and Singh 1978)

$$MD^e_{xy} = \frac{C'}{2} \left\{ \sum_{\mathbf{g}} \frac{(g-q)_x(g-q)_y S(\mathbf{g}-\mathbf{q})F(g-q)}{(g-q)^2 + F(g-q)/a^2} \right\},$$ (5)

where C' is an adjustable constant related to the bulk modulus K_e of the electron gas, $\mathbf{g}$ is a reciprocal lattice vector and $S(\eta)$ is the interference factor defined by

$$S(\eta) = \int_{\Omega} \exp(i\eta \cdot \mathbf{r}) d\Omega/\Omega,$$ (6)

and has been evaluated exactly over the actual shape of the atomic polyhedron for the bcc lattice (Ramamurthy 1978). $F(\eta)$ is a screening function which is determined by the choice of the screening approximation. A large number of expressions exist in literature and the following three expressions were used for $F(\eta)$ in the present work:
(i) the simple random-phase approximation

$$F(\eta) = F_0(\eta) = \frac{a^2 K_s^2}{2} \left[1 + \frac{4K_F^2 - \eta^2}{4K_F\eta} \ln \left| \frac{2K_F + \eta}{2K_F - \eta} \right| \right],$$ (7)

where K_s and K_F are the Thomas-Fermi screening parameter and the Fermi wavevector, respectively;
(ii) the Vashishta-Singwi (1972) approximation

$$F(\eta) = F_0(\eta) \left[1 - \frac{F_0(\eta)A}{a^2\eta^2} \{ 1 - \exp[-B(\eta/K_F)^2] \} \right]^{-1},$$ (8)

where the values of the constants A and B for alkali metals are given in table 2;
(iii) the Taylor (1978) approximation

$$F(\eta) = F_0(\eta) \left[1 - \frac{F_0(\eta)}{4a^2K_F^2} \{ 1 + 0.1534 K_s^2/4K_F^2 \} \right]^{-1},$$ (9)

which satisfies the compressibility sum rule exactly.

The first term on the right side of (5) corresponding to $\mathbf{g} = 0$ represents the contribution from normal processes to the elements of D^e. Since these expressions do not affect the transverse modes of vibration, a model which does not include the contributions from the umklapp processes to the electron-ion interactions fails to satisfy the symmetry requirements of the lattice. The evaluation of the interference factor in (6) over the actual shape of the Wigner-Seitz cell (Sharan *et al* 1973; Goel *et al* 1975; Ramamurthy and Neelakandan 1977) hardly serves any purpose especially when the umklapp processes are ignored. In the present investigation nearly 250 terms representing the contribution of umklapp processes associated with several reciprocal lattice vectors are included in the sum, and the elements of D^e so obtained are consistent with the translational symmetry of the lattice as they contribute to the longitudinal as well as the transverse modes of vibrations. These expressions also reduce to a convenient form because the exact evaluation of (6) yields

$$S(\eta) = 0 \quad \text{when} \quad \eta = \mathbf{g} \neq 0.$$ (10)

2.2 *Force constant evaluation*

The experimental values of three elastic constants and four zone boundary frequencies along the principal symmetry directions of the crystal are needed to evaluate seven force constants that appear in the dynamical matrix elements. For this purpose, the elastic constants are expressed in terms of these force constants by comparing the secular determinant in the long wavelength limit with the elastic determinant. These are given by

$$aC_{11} = \tfrac{2}{3}\beta_1 + 2\beta_2 + 4\beta_3 + 8\gamma_1 + 4\gamma_2 + 6\gamma_3 + C', \tag{11a}$$

$$aC_{12} = \tfrac{2}{3}\beta_1 + 2\beta_3 - 4\gamma_1 - 2\gamma_2 - 3\gamma_3 + C' \tag{11b}$$

and

$$aC_{44} = \tfrac{2}{3}\beta_1 + 2\beta_3 + \tfrac{4}{3}\gamma_1 + 6\gamma_2 + 6\gamma_3. \tag{11c}$$

In addition, the symmetry associated with the zone boundary points (100), $(\tfrac{1}{2}\tfrac{1}{2}0)$ and $(\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2})$ is exploited to obtain relevant relations between these frequencies and the force constants by solving the secular determinant. These are given by

$$4\pi^2 M v_L^2(100) \equiv 4\pi^2 M v_T^2(100) = \tfrac{16}{3}(\beta_1 + 4\gamma_1 + 6\gamma_2) + \frac{C'}{2}SL(100), \tag{12a}$$

$$4\pi^2 M v_L^2(\tfrac{1}{2}\tfrac{1}{2}0) = 4(\tfrac{4}{3}\beta_1 + \beta_2 + \beta_3 + \tfrac{10}{3}\gamma_1 + 7\gamma_2 + 3\gamma_3) + \frac{C'}{2}SL(\tfrac{1}{2}\tfrac{1}{2}0), \tag{12b}$$

$$4\pi^2 M v_{T_1}^2(\tfrac{1}{2}\tfrac{1}{2}0) = 4(\beta_2 + 6\gamma_1 + 3\gamma_2 + 3\gamma_3) + \frac{C'}{2}ST_1(\tfrac{1}{2}\tfrac{1}{2}0), \tag{12c}$$

$$4\pi^2 M v_{T_2}^2(\tfrac{1}{2}\tfrac{1}{2}0) = \frac{8}{3}(\beta_1 + 3\beta_3 + 2\gamma_1 + 9\gamma_2) + \frac{C'}{2}ST_2(\tfrac{1}{2}\tfrac{1}{2}0), \tag{12d}$$

and

$$4\pi^2 M v_L^2(\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}) \equiv 4\pi^2 M v_T^2(\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}) = 4(\tfrac{2}{3}\beta_1 + \beta_2 + 4\gamma_1 + 6\gamma_2)$$
$$+ \frac{C'}{2}SL(\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}), \tag{12e}$$

where $SL(100)$, $SL(\tfrac{1}{2}\tfrac{1}{2}0)$, $ST_1(\tfrac{1}{2}\tfrac{1}{2}0)$, $ST_2(\tfrac{1}{2}\tfrac{1}{2}0)$ and $SL(\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2})$ correspond to umklapp contributions to the appropriate modes of vibrations, represented by { } in (5) which is summed over several reciprocal lattice vectors including $\mathbf{g} = 0$ at the respective zone boundary points.

In the present investigations, the number of force constants of the CGW model is reduced to six by neglecting the third neighbour central force constant, β_3 in order to avoid the use of any transverse zone boundary frequencies along the $[\zeta\zeta 0]$ direction, in their evaluation. These constants have been evaluated uniquely by making use of the remaining frequencies and elastic constants. The experimental values of the elastic constants along with the atomic mass and lattice parameter of all alkali metals are given in table 1 and the corresponding values of the three zone boundary frequencies as well as the values of the constants A and B appearing in (8) are given in table 2. Numerical values of the force constants, calculated using these data in lithium, sodium, potassium, rubidium and cesium are listed in table 3.

Table 1. Atomic mass, lattice parameter and elastic constants of alkali metals.

Metal	M (10^{-27}kg)	a (10^{-10}m)	C_{11}	C_{12}	C_{44}	Reference
			(10^{10}Nm^{-2})			
Lithium	11·65	3·484	1·435	1·208	1·075	Slotwinski and Trivisonno (1969)
Sodium	38·18	4·240	0·816	0·679	0·570	Diederich and Trivisonno (1966)
Potassium	64·91	5·226	0·415	0·340	0·284	Marquardt and Trivisonno (1965)
Rubidium	142·00	5·628	0·312	0·262	0·186	Gutman and Trivisonno (1967)
Cesium	220·70	6·050	0·247	0·206	0·148	Kollarits and Trivisonno (1968)

Table 2. Screening constants and experimental zone boundary frequencies of alkali metals.

| Metal	A^*	B^*	$v_L(100)$	$v_L(\tfrac{1}{2}\tfrac{1}{2}0)$	$v_L(\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2})$	Reference
			THz			
Lithium	1·007	0·299	8·800	9·150	7·000	Smith *et al* (1968)
Sodium	1·078	0·286	3·580	3·890	2·880	Woods *et al* (1962)
Potassium	1·167	0·271	2·210	2·380	1·780	Cowley *et al* (1966)
Rubidium	1·198	0·266	1·320	1·445	1·110	Copley and Brockhouse (1973)
Cesium	1·235	0·260	0·943	1·054	0·789	Ramamurthy and Satishkumar (1981)**

*Vashishta and Singwi (1972);   **Homologous frequencies.

Table 3. Force constants of alkali metals (in 10^{-3}Nm^{-1}).

Metal	β_1	β_2	γ_1	γ_2	γ_3	C'
Lithium	1747	−266	−127	426	33	3485
Sodium	3658	736	−79	24	−11	143
Potassium	2020	399	−50	38	−4	294
Rubidium	1328	379	−58	46	−7	430
Cesium	1125	344	−57	29	7	347

3. Results

The phonon frequencies of lithium, sodium, potassium, rubidium and cesium have been calculated by solving the secular determinant along the principal symmetry directions of the crystal as well as at 47 selected wave vectors spread over the reduced Brillouin zone using three different screening functions *viz* (7), (8) and (9) for $F(\eta)$ in the evaluation of the force constants. The evaluation of β_3 or the use of different sets of zone boundary frequencies or elastic constants in the evaluation of other force constants was precluded by the large experimental errors associated with the smaller zone boundary frequencies, $v_{T_1}(\frac{1}{2}\frac{1}{2}0)$ and $v_{T_2}(\frac{1}{2}\frac{1}{2}0)$. The numerical values of the force constants are altered with the screening function. Nevertheless, it was observed that the phonon frequencies derived from the three sets of force constants are not significantly different from each other and therefore only the results obtained from the set shown in table 3 are presented here. The dispersion curves of lithium, sodium, potassium, rubidium and cesium obtained by plotting their phonon frequencies as a function of reduced wave vector, ζ along the principal symmetry directions are shown in figures 1–3 respectively. Further, the experimental phonon frequencies of lithium,
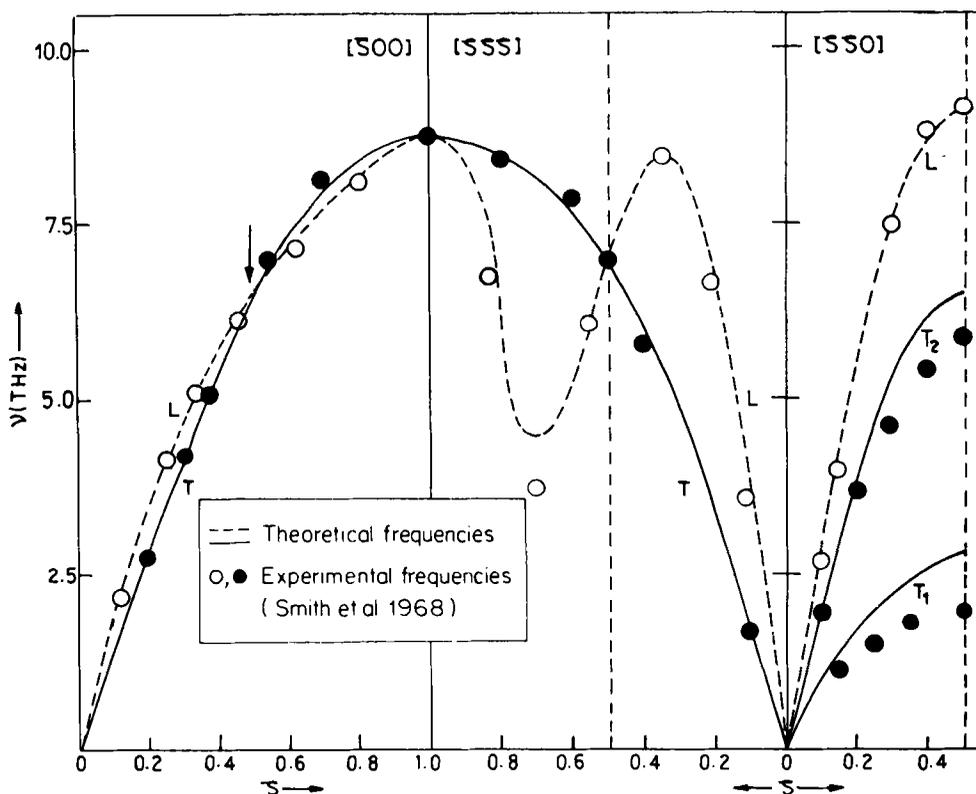
Figure 1. Dispersion curves of lithium along the principal symmetry directions. The arrow indicates the wavevector $\zeta_c = 0.49$ at which the L and T branches crossover along the $[\zeta 00]$ direction.
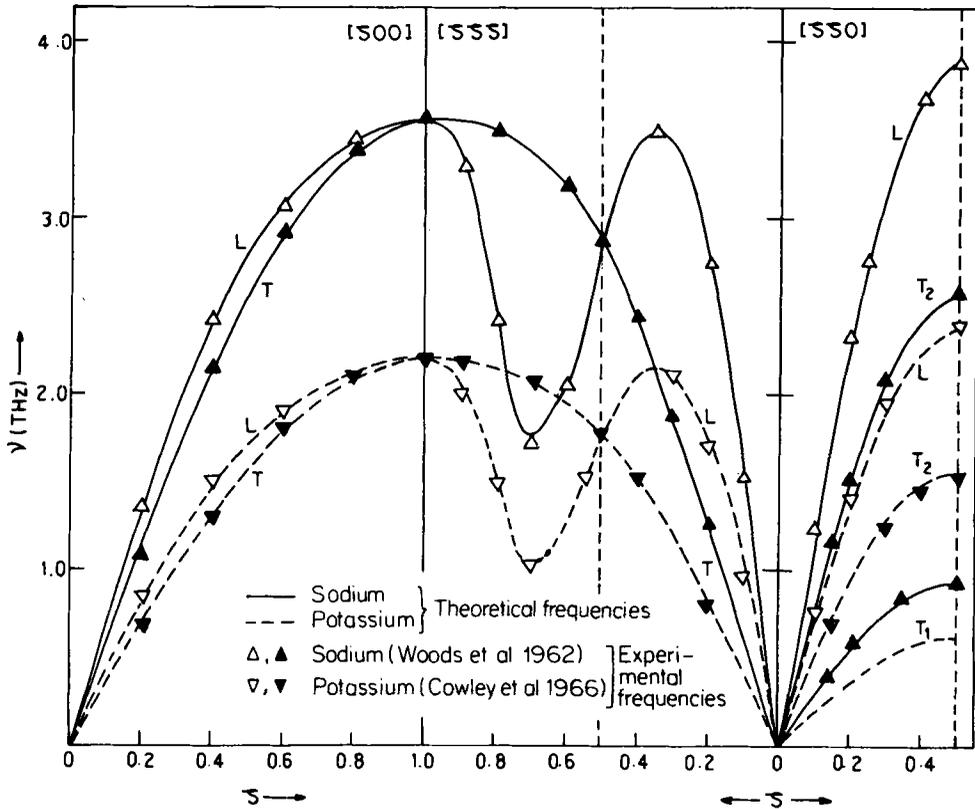
Figure 2. Dispersion curves of sodium and potassium along the principal symmetry directions.

sodium, potassium and rubidium as well as the homologous phonon frequencies of cesium are plotted as a function of ζ in all these figures to facilitate their comparison with the present theoretical frequencies.

The phonon frequency distribution function, $G(v)$ has been determined by dividing the Brillouin zone into $10 \times 10 \times 10$ parts and giving the proper statistical weight to each of the frequencies calculated at the 47 irreducible wavevectors. In order to get approximately the same number of frequency intervals, the entire frequency range of lithium is divided into intervals of 0.25 THz, that of sodium and potassium into intervals of 0.1 THz whereas that of rubidium and cesium is divided into intervals of 0.05 THz. The phonon frequency histograms of alkali metals, obtained by root sampling technique (Dayal and Sharan 1960, 1961) have been made use of in the evaluation of their lattice specific heats in the temperature range 5–160 K. The equivalent Debye temperature, θ_D calculated from the theoretical values of lattice specific heat is plotted as a function of temperature for lithium, sodium and potassium, rubidium and cesium in figures 4a, b, c respectively. Besides, θ_D values, calculated from the experimental values of lattice specific heats of all alkali metals (Krier *et al* 1957; Martin 1960; Filby and Martin 1965) obtained after subtracting the electronic contributions as well as the theoretical values of the lattice specific heats of lithium,
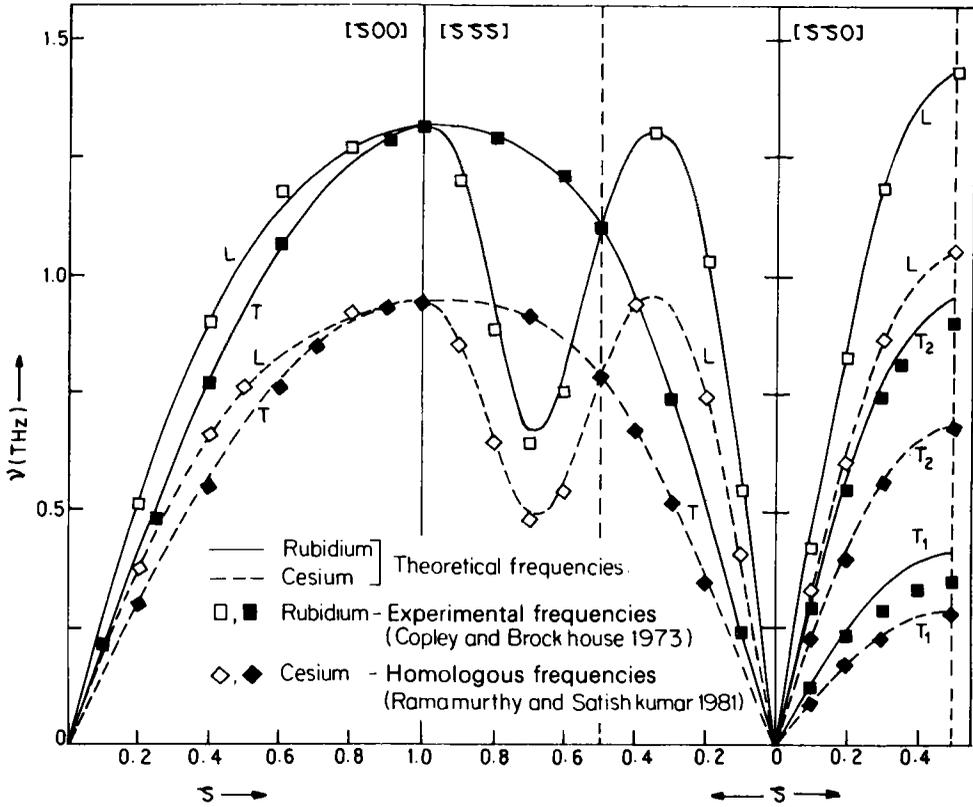
Figure 3. Dispersion curves of rubidium and cesium along the principal symmetry directions.

sodium and potassium deduced on the basis of a CGW model which does not satisfy the translational symmetry of the lattice (Ashokkumar 1973; Sharan *et al* 1973) are shown in the respective figures to facilitate their comparison with the present values.

4. Discussion

It is obvious from figure 1 that the longitudinal branch of lithium crosses over the transverse branch at $\zeta \sim 0.49$ and then becomes degenerate with the latter at the zone boundary point, (1 0 0). On the contrary, figures 2 and 3 show that the corresponding branches of sodium, potassium, rubidium and cesium do not crossover at any wavevector and they do degenerate at (1 0 0). Further, the transverse and longitudinal branches of all alkali metals along the $[\zeta\zeta\zeta]$ direction degenerate at the point $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$. It should therefore be clear from these figures that the CGW model has succeeded in reproducing the crossover in lithium at a wavevector which is not very much different from its experimental value of 0.46, without producing any crossover in other alkali metals as well as the degeneracies at (1 0 0) and $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ which are consistent with the symmetry requirements of the lattice. In addition, the theoretical
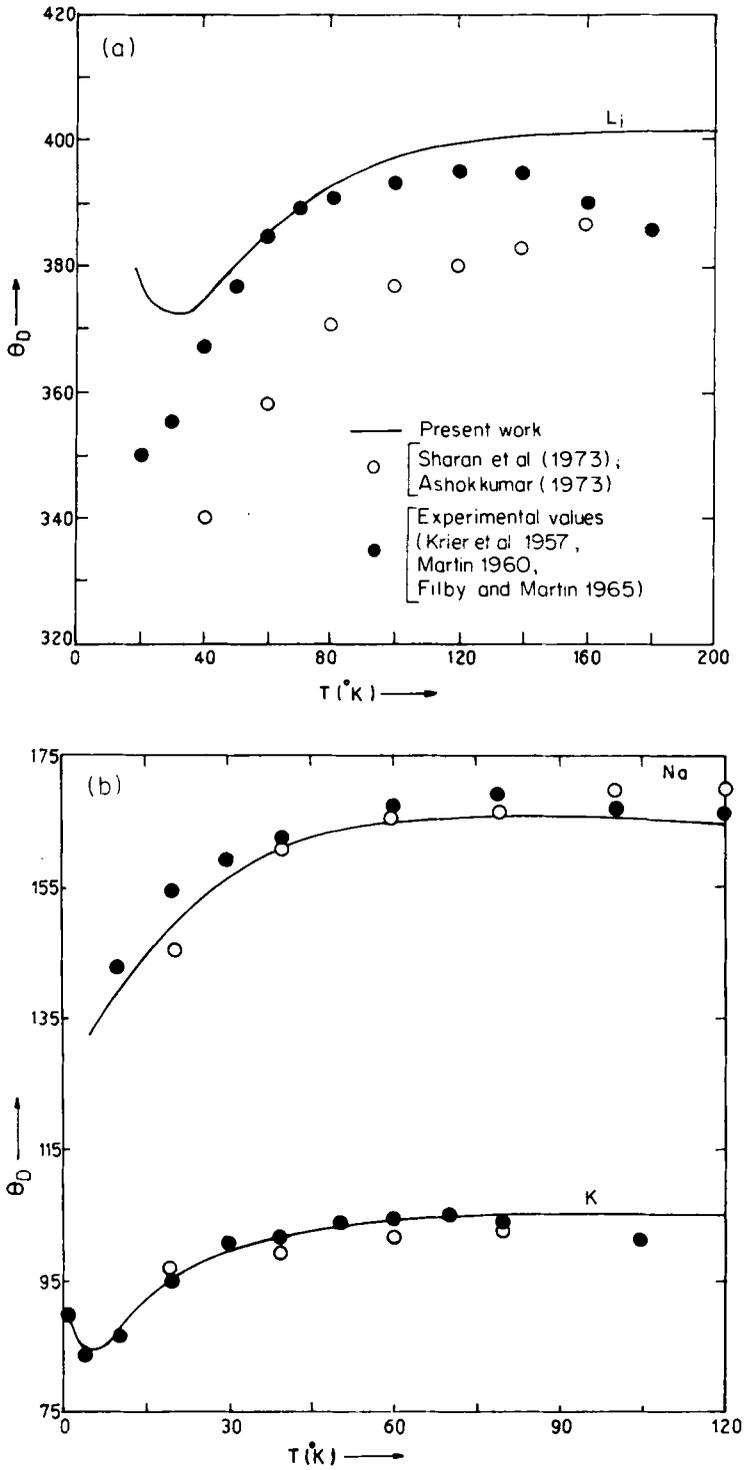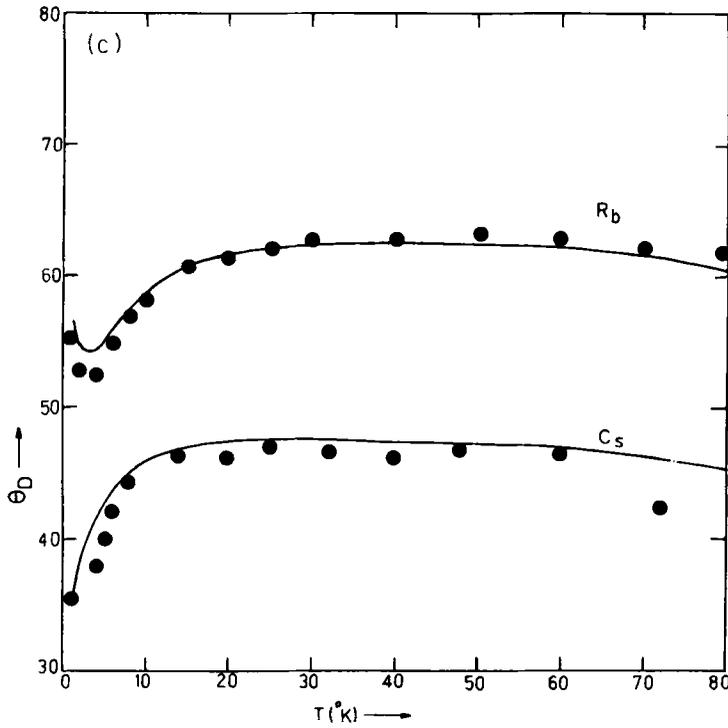
Figure 4.

Figure 4. θ_D-T curves of **a.** lithium, **b.** sodium and potassium **c.** rubidium and cesium.

phonon frequencies and the corresponding experimental or homologous phonon frequencies of alkali metals are in excellent agreement with each other at all wave vectors and polarizations. The maximum discrepancies between the two is $< 5\%$, which is of the same order as the uncertainties associated with these calculations, but some transverse frequencies of lithium and rubidium along $[\zeta\zeta 0]$ direction are an exception. On the other hand, no lattice dynamical model has so far succeeded in deducing the actual phonon frequencies at all wave vectors along the $[\zeta\zeta 0] T_1$ and $[\zeta\zeta 0] T_2$ branches. It is precisely because of this reason that these zone boundary frequencies were not made use of in the evaluation of the force constants of the present model or many other models. Further, the phonon frequencies of $[\zeta\zeta 0] T_1$ being small, they could not be measured in the case of potassium (Cowley *et al* 1966) while their measurements in other alkali metals were invariably associated with large errors. In view of this, the apparent differences between the experimental and theoretical frequencies of these branches are not really significant. Hence the lattice dynamical results of this unified study are far more reliable than those of earlier studies based on deficient models and confined to two or three alkali metals.

The success of the present CGW model which incorporates some three-body interactions, in reproducing very accurately the experimental dispersion curves of all alkali metals, including the crossover in lithium implies that there is hardly any variation in the nature or range of their interatomic forces and thus provides additional support to the existence of homology among their phonon frequencies (Ramamurthy and Satishkumar 1978, 1980). However, the numerical values of the angular force

constants, listed in table 3, seem to suggest that the three-body interactions of the CGW model are not really important in the case of alkali metals and hence they are incapable of producing a crossover in lithium along the $[\zeta 00]$ direction. On the contrary, the umklapp processes which were included to restore translational symmetry to the CGW model, play a significant role in the success of the unified approach to the lattice dynamics of alkali metals. For instance, umklapp contribution to the transverse modes of vibration increases faster, with the wavevector along the $[\zeta 00]$ direction, than the normal and umklapp contributions to the longitudinal modes of vibration (Ramamurthy and Singh 1978). Besides, it is obvious from table 3 that the numerical value of C' which represents the strength of the electron-ion interactions, associated with lithium is an order of magnitude larger than those associated with other alkali metals. Larger values of C' in turn give rise to larger excess umklapp contributions to the transverse modes which become equal to and greater than the excess ion-ion contributions to the longitudinal modes, respectively, at and above some wavevector, ζ_c and the two branches of lithium crossover at that wavevector. On the other hand, smaller excess umklapp contributions to the former can never match the excess ion-ion interactions to the latter at any wavevector and hence the dispersion curves of other alkali metals do not crossover.

It should therefore be obvious from this discussion that the phonon dispersion curves of lithium in general and their crossover along the $[\zeta 00]$ direction in particular, are highly sensitive to the manner in which the umklapp processes are incorporated into a lattice dynamical model whereas those of other alkali metals, with weak electron-ion interactions, are not. Consequently, the neglect of umklapp contributions which invariably destroys the translational symmetry (Tripathi and Behari 1971; Sharan et al 1973; Goel et al 1975; Rai and Hemkar 1977; Gohel and Jani 1979; Khanna and Rathore 1979), their erroneous evaluation arising out of approximating the atomic polyhedron by a sphere of equivalent volume in (6) (Dacunha Lima et al 1974; Singh et al 1976; Bonelli and Shukla 1977; Sharma and Awasthi 1979) or ignoring the volume forces altogether (Cavalheiro and Shukla 1974; Prakash et al 1974; Goel and Dayal 1977; Bonelli et al 1979; Khanna and Rathore 1979) resulted in the failure of earlier models to reproduce the phonon dispersion curves of lithium. The success of the present investigations clearly establishes that the observed crossover in lithium is not an anomalous property and the failure of a variety of force constant models to reproduce it should be attributed to their intrinsic deficiencies rather than to the variation in the nature or range of atomic interactions in alkali metals. Besides, the reproduction of the experimental crossover in lithium along the $[\zeta 00]$ direction by the earlier AS models (Ramamurthy and Singh 1978; Satishkumar 1981) as well as by the present CGW model proves convincingly that the strong electron-ion interactions manifest themselves as a crossover in an alkali metal and the three-body angular interactions have nothing to do with it. However, the strength of the electron-ion interactions, represented by C' is highly sensitive to the differences in the assumptions regarding the nature and range of the ion-ion interactions. It is not at all clear from the present investigations whether all lattice dynamical models produce a crossover in lithium when they incorporate the same volume forces. Hence it is essential to understand the role played by the ion-ion interactions in producing a crossover, by comparing a variety of force constant models which are free from any basic inadequacies. The results of this analysis are reported elsewhere (Ramamurthy and Satishkumar 1984).

Figures 4a–c clearly show that the theoretical values of θ_D are in very good agreement

with the corresponding experimental values, the maximum discrepancy between the two being $< 4\%$ in all cases. It is therefore reasonable to conclude that the unified study based on the CGW model reproduces the experimental lattice specific heats of all alkali metals over a wide temperature range. On the other hand, θ_D values of lithium calculated by Sharan *et al* (1973) are in poor agreement with the experimental as well as the present theoretical values at all temperatures whereas those of sodium and potassium (Ashokkumar 1973) are in excellent agreement with the latter values. It is, however, necessary to point out that these authors subtracted, wrongly, the electronic contributions to the specific heat from their theoretical lattice specific heats before deducing the Debye temperatures. As a consequence, the correct θ_D values shown in figures 4(a) and (b) are lower than those actually obtained by Sharan *et al* (1973) and Ashokkumar (1973). Besides, these authors deduced the vibrational spectra of lithium, sodium and potassium on the basis of a CGW model which does not conform to the translational symmetry of the lattice. The neglect of umklapp processes together with the negative C' values lower the θ_D values significantly in the case of lithium but they hardly have any effect on the θ_D values of the other alkali metals. Hence the success of the present investigations in reproducing the experimental data on lattice specific heats of all alkali metals should be attributed to the incorporation of the umklapp contributions rather than the three-body angular forces in the CGW model. Nevertheless, there are differences between the theoretical and experimental θ_D values at very low as well as at very high temperatures. The specific heat calculations using sampling technique are unsatisfactory at very low temperatures. Besides, lithium and sodium undergo martensitic transformation at 76 K and 36 K, respectively. Experimental values of specific heats below these temperatures correspond to hcp structure or a mixture of bcc and hcp structures. The apparent discrepancies between experimental and theoretical values in this region cannot, therefore, be attributed to the failure of the CGW model. On the other hand, the anharmonic effects which are responsible for thermal expansion become important at high temperatures and the experimental values of θ_D decrease with temperature. The present lattice dynamical model is incapable of reproducing these effects.

5. Conclusions

It is obvious that the CGW model has reproduced the experimental dispersion curves of lithium, sodium, potassium, rubidium and the homologous dispersion curves of cesium as well as the experimental θ_D-T curves of all alkali metals, very accurately, by incorporating the volume forces which satisfy the symmetry requirements of the lattice. The dispersion curves of an alkali metal crossover when the excess ion-ion contributions to the longitudinal vibrations are compensated by the excess umklapp contributions to the transverse vibrations at some wavevector along $[\zeta 00]$ direction. Larger values of C', corresponding to stronger electron-ion interactions, reproduce the observed crossover in lithium while smaller C' values supress it in other alkali metals. Besides the θ_D values of the former are lowered whereas those of the latter are unaffected by the neglect of the umklapp processes. However, the three-body interactions of the CGW model are of no consequence in the lattice dynamical study of alkali metals. The success of this unified study invariably leads to the conclusion that there is hardly any variation in the nature or range of interatomic forces of alkali metals.

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